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Separation of the oligomeric silsesquioxanes $(\text{HSiO}_{3/2})_{8-18}$ by size-exclusion chromatography

HERIBERT BÜRGI and GION CALZAFERRI*

Institute for Inorganic and Physical Chemistry, University of Berne, CH-3000 Berne 9 (Switzerland)

SUMMARY

The spherical siloxanes $(\text{HSiO}_{3/2})_n$ ($n = 8-18$) have been separated by size-exclusion chromatography, a technique that allows for preparative separations. These molecules are ideal test-cases for the hard-sphere solute size-exclusion retention theory because of their nearly identical chemical behaviour and their nearly ideal spherical structure.

INTRODUCTION

Spherical siloxanes with the general formula $(\text{RSiO}_{3/2})_n$ are called silsesquioxanes and abbreviated as RT_n . Frye and Collins¹ reported the synthesis of the simplest silsesquioxane molecules namely HT10–HT16, which always leads to a mixture. For our intentions, however, we need the silsesquioxanes as pure as possible²⁻⁴. It is difficult to separate them because of their similar properties (solubility, sublimation temperature, etc.).

The appropriate tool for separation seems to be size-exclusion chromatography (SEC), also called gel permeation chromatography.

EXPERIMENTAL

The silsesquioxanes were synthesized as described previously¹. A solution of 9.5 ml of HSiCl_3 in 150 ml of benzene was slowly added to a solution of 200 ml of benzene containing 43 ml of concentrated H_2SO_4 and 31 ml of fuming H_2SO_4 . The product was recrystallized in tetrahydrofuran (THF). While the main by-product gelled in THF, the desired products remain in solution. The chromatogram of the products in Fig. 1D shows that the reaction yields not only HT10–HT16 but also HT18.

We tried the same synthesis with toluene as solvent. To our surprise we have obtained not only HT10–HT18 as in the benzene-based synthesis but also HT8. The result of this experiment is illustrated in Fig. 1C.

The separation was performed on a PLGel column (600 × 7.5 mm I.D., 50 Å pore diameter, 5- μm particle size, Polymer Labs., Shropshire, U.K.). The HPLC system consisted of an Erma ERC 3511 on-line degasser, a Merck–Hitachi LC 6200

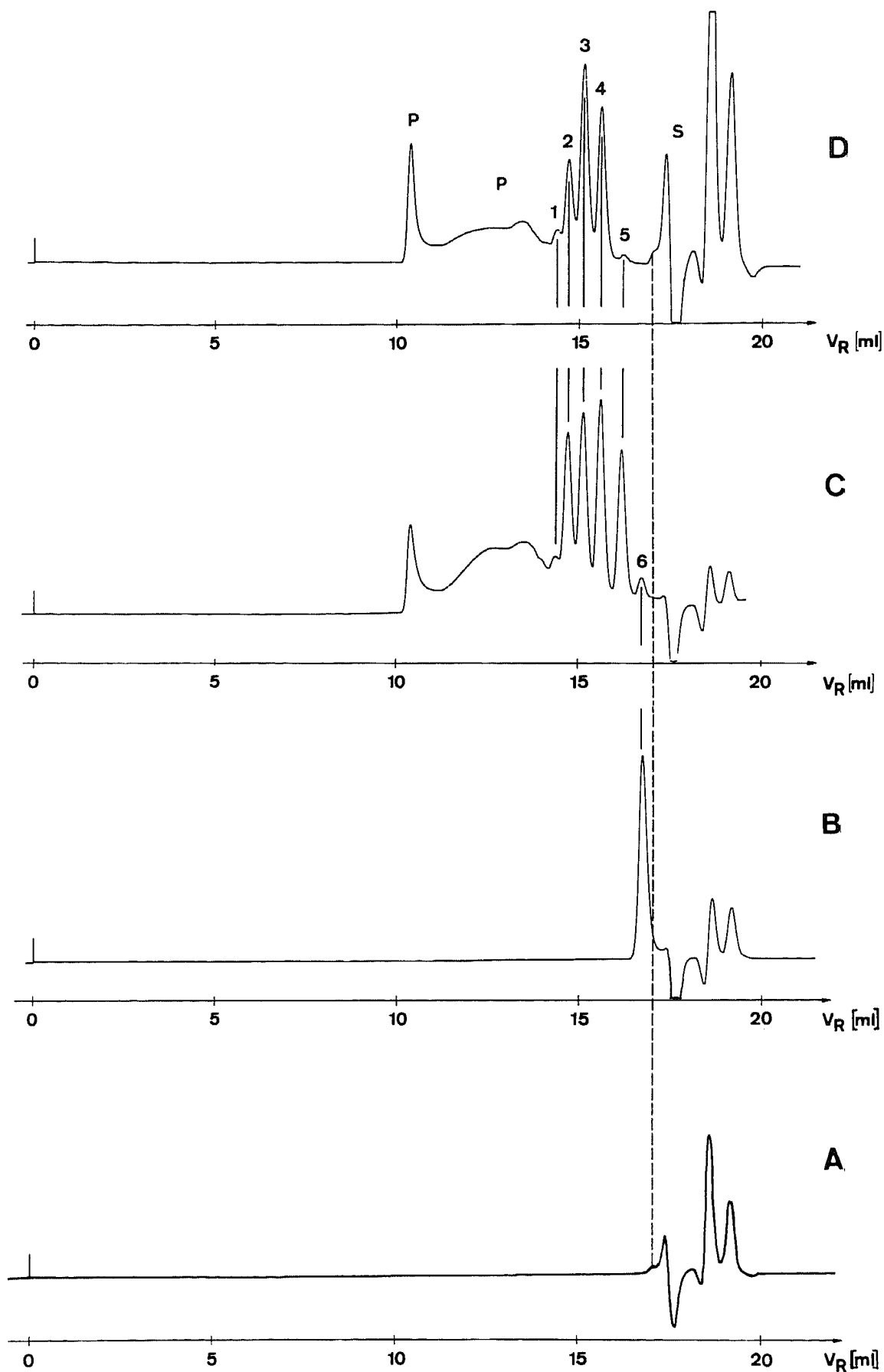


Fig. 1. Comparison of chromatograms in hexane. Peaks: P = polymer; S = solvent; 1 = HT18; 2 = HT16; 3 = HT14; 4 = HT12; 5 = HT10; 6 = HT8. (A) Solvent: hexane fraction that was used as solvent for all samples. (B) Pure HT8; peaks on and to the right of the dashed line belong to the solvent. (C) Products of the synthesis in toluene: peak 6 = HT8 appears. (D) Products of the synthesis in benzene: peak 6 = HT8 is absent.

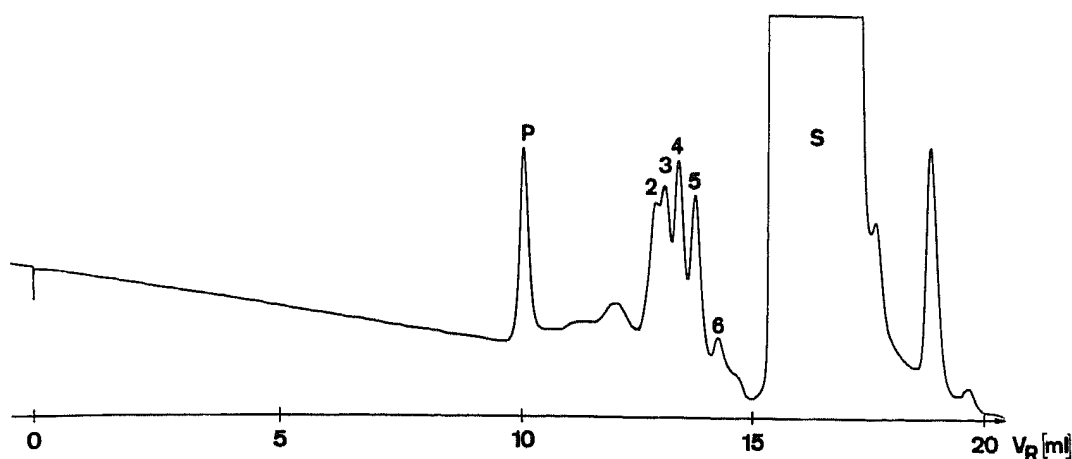


Fig. 2. Chromatogram of the same synthesis products as in Fig. 1D but with toluene as eluent. HT18 does not appear.

pump, the column and an Erma ERC 7512 refractive index detector. The chromatograms were recorded with an HP 3396A integrator. Toluene (Merck p.A.) and hexane fraction for high-performance liquid chromatography (HPLC) (Romil Chemicals) were used as mobile phase. To observe the chromatograms shown in Figs. 1 and 2 the flow-rate was 1 ml/min and the injected sample amount was 20 μ l of saturated silsesquioxane solution in hexane.

RESULTS

The chromatograms show significant differences between hexane and toluene as mobile phase (Figs. 1 and 2). The retention volumes for the identified compounds with hexane as mobile phase are listed in Table I.

The peaks were separated and identified by mass spectrometry and infrared and ^1H and ^{29}Si nuclear magnetic resonance spectroscopy.

DISCUSSION

Assuming the absence of adsorption, the SEC retention volume V_R can be expressed⁷ as:

$$V_R = V_0 + K_{\text{SEC}} V_i \quad (1)$$

where

K_{SEC} = equilibrium constant for the SEC process representing the ratio of the average solute concentration in the pores to that outside the pores.

V_i = stagnant part of the mobile phase (pore volume);

V_0 = moving part of the mobile phase (interstitial volume).

To determine K_{SEC} accurately, one has to set the total exclusion limit and the total permeation limit with $K_{\text{SEC}} = 0$ and $K_{\text{SEC}} = 1$, respectively. The total exclusion limit is determined by the large polycondensates, the first peak in the chromatograms. The total permeation limit has been determined with hexane (Fig. 1A). Because of differences in temperature and air saturation, it is possible to apply a refractive index detector for the detection of hexane in hexane as mobile phase.

TABLE I
RETENTION VOLUMES IN HEXANE AS MOBILE PHASE

Molecule	Retention volume (ml)
HT18	14.23
HT16	14.57
HT14	14.98
HT12	15.45
HT10	16.01
HT8	16.55

Hence the total exclusion limit for our analytical column was determined to be $V_R(K_{SEC} = 0) = 10.28$ ml and the total permeation limit is $V_R(K_{SEC} = 1) = 18.94$ ml. From this we get $V_0 = 10.28$ and $V_i = 8.66$ ml.

Fig. 2 shows a chromatogram obtained with toluene, to illustrate the different behaviour of the two mobile phases toluene and hexane. Comparison of the data in Figs. 1 and 2 illustrates clearly that the resolution is far better in hexane than in toluene.

MOLECULAR GEOMETRY CALCULATIONS

According to the hard-sphere solute model⁷, the solute-pore interaction can be described by geometrical considerations. Several relationships for the distribution coefficient K_e can be derived, depending on the pore shape:

$$\text{Cylindrical pores } K_e = \left(1 - \frac{r}{\bar{a}_c}\right)^2 \quad (2)$$

$$\text{Spherical pores } K_e = \left(1 - \frac{2r}{3\bar{a}_s}\right)^3 \quad (3)$$

$$\text{Random-plane pores } K_e = \exp\left(-\frac{2r}{\bar{a}_e}\right) \quad (4)$$

$$\text{where } \bar{a} = \frac{2 \times \text{pore volume}}{\text{pore surface area}}$$

$$r = \text{radius of a solute molecule;} \\ \bar{a}_c, \bar{a}_s, \bar{a}_e = \text{radii of the pores.}$$

Neglecting the solute molecule packing interaction, $K_e = K_{SEC}$, it is possible to calculate the radius of every HTn molecule by assuming cylindrical pores. The value of r can be calculated from eqn. 2 if we accept the manufacturers' specification of 25 Å for \bar{a}_c . K_{SEC} is calculated from eqn. 1 by applying the experimentally determined values of V_0 , V_i and the retention volume V_R and the retention volume V_R (Table I). The radius r_{struct} of HT8 has been determined from X-ray structural data^{8,9}, assuming the Van der Waals radius of H to be 1.2 Å. For the other molecules r_{struct} was calculated from

TABLE II

VALUES FOR THE EQUILIBRIUM CONSTANTS AND CALCULATED AND STRUCTURAL MOLECULAR RADII

<i>Molecule</i>	K_{SEC}	r (\AA)	r_{struct} (\AA)
HT8	0.7237	3.7	4.8
HT10	0.6614	4.7	5.5
HT12	0.5968	5.7	6.1
HT14	0.5425	6.6	6.8
HT16	0.4952	7.4	7.5
HT18	0.4559	8.1	8.2

geometrical construction, by applying the same Si–O–Si distances as in HT8. The results are reported in Table II.

The radii calculated for HT8 and HT10 are too small whereas the radii of the other molecules fit perfectly well with r_{struct} . This could be because the smaller molecules "see" a somewhat larger pore size because of non-idealities of the pore-shape.

It is interesting to try the reverse and to calculate the pore size from r_{struct} and K_{SEC} for the different pore-shapes. The results are reported in Table III. HT8 and HT10 lead in each case to a too large pore volume. For cylindrical pores, however, the pore volume converges very well to the expected 25 \AA . We conclude that the cylindrical pore-shape model fits best to our data, and that HT8 and HT10 are so small that they "see" the non-idealities of the pores, which means that they "feel" a somewhat larger cage.

TABLE III

VALUES OF THE PORE RADII, CALCULATED FROM r_{struct} AND K_{SEC}

<i>Molecule</i>	\bar{a}_c (\AA)	\bar{a}_s (\AA)	\bar{a}_e (\AA)
HT8	32.1	31.3	29.7
HT10	29.4	28.5	26.6
HT12	26.8	25.7	23.6
HT14	25.8	24.6	22.2
HT16	25.3	23.9	21.3
HT18	25.2	23.7	20.9

CONCLUSION

We have demonstrated that SEC is an appropriate tool for separating the different HT n ($n = 8-18$). These molecules seem to be ideal test-cases for advancing the SEC retention theory because of their nearly identical chemical behaviour and their nearly ideal spherical structure^{5,6}. It is very satisfactory that the simple hard-sphere

solute model seems to work well for describing the separation process of these molecules.

ACKNOWLEDGEMENTS

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